

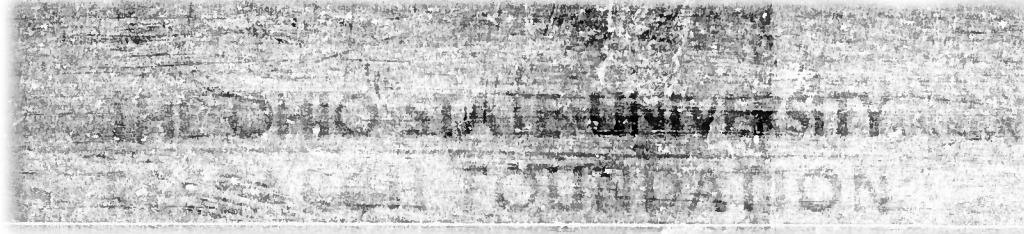
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Subject of Report Part IV of Final Report.
The Preparation, Properties
and Crystal Structure
of Tricesium Monoxide.

Submitted by Khi-Ruey Teai.

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FINAL REPORT PART IV

THE PREPARATION, PROPERTIES AND CRYSTAL
STRUCTURE OF TRICESIUM MONOXIDE

by Khi-Ruey Tsai

I. INTRODUCTION

The existence of four suboxides of cesium, Cs_7O , Cs_4O , Cs_7O_2 , and Cs_3O , was first discovered by Rengade⁴ through determination of temperature composition diagrams early in 1909. More recently, Brauer¹ substantiated a part of the phase diagram by measurement of the resistivity-temperature coefficients at various compositions ranging from pure cesium to $CsO_{0.25}$. He also checked the phase transitions from the x-ray powder diagrams of the samples. He observed, however, that the higher suboxides of cesium gave abnormal x-ray powder patterns consisting of only a few lines.

It is to be noted here that none of the higher suboxides, Cs_4O , Cs_7O_2 , and Cs_3O , has ever been prepared and isolated in a sufficiently pure state for x-ray characterization, probably mainly because of the difficulty of handling such extremely reactive materials. The usual method¹ of preparing cesium suboxides by direct combination of pure cesium and pure oxygen also appears to have the following difficulties in the case of preparing the higher-melting suboxides, Cs_7O_2 and Cs_3O : (1) The reaction temperature must be raised above the melting point of the partially oxidized metal after each addition of the oxygen towards the later stage of the oxidation (approximately 120°C in the case of Cs_7O_2 and 170°C in the case of Cs_3O); otherwise a dark surface layer of higher oxides will be formed and this will practically stop further absorption of oxygen. (2) On the other hand, at such high temperatures, an appreciable amount of the cesium will be vaporized and oxidized essentially in the vapor phase to higher oxides. These will be deposited as thin films above the main reaction product. (In one experiment, carried out in this laboratory, the uppermost film was found to consist of pure, yellow cesium superoxide, CsO_2 , identified by its x-ray powder pattern. On exposure to cesium vapors from the molten suboxide, the yellowish film gradually became reddish and finally completely darkened.)

In the present work, these difficulties were overcome by oxidizing pure cesium to Cs₃O with the calculated amount of pure oxygen admixed with about 0.2 mm of purified argon. The presence of this small amount of inert gas allowed the final reaction temperature to be raised to 170°C without excessive vaporization of the volatile metal.

In this way, samples of Cs₃O were obtained in dark greenish, translucent chips, having metallic luster, soft and malleable and therefore difficult to pulverize. The following physical properties were observed: (1) melting point: Ca. 165°C, as observed in pyrex capillary. (2) Density: 2.73 ± 0.03 g/cc. at 30.2°C, as determined by displacement of dried, oxygen-free toluene. (3) Magnetic susceptibility at 30°C: 0.15 × 10⁻⁶ cgs units per gram, or 61 × 10⁻⁶ cgs units per mol, as compared with -(2 × 35 × 10) × 10⁻⁶ + 29 × 10⁻⁶ - 51 × 10⁻⁶ cgs units per mol calculated from Wiedeman's law for Cs₂O₄Cs, and with $\chi_m = 29 \times 10^{-6}$ for metallic cesium. Thus the suboxide of cesium, like metallic cesium itself, is weakly paramagnetic. But the large deviation between the observed paramagnetic susceptibility and that calculated from Wiedeman's law for Cs₂O₄Cs suggests that the suboxide is probably not a lattice compound of metallic cesium in the layer lattice of Cs₂O. The magnetic measurement was done by the standard method, using the apparatus recently described by Harris and Lindenmeyer. (4) Electrical resistivity at 300°C: 7.21 × 10⁻² ohm-cm, as compared with 3.66 × 10⁻² ohm-cm for metallic cesium. Resistivity-temperature coefficient: 0.0025. The measurement was done potentiometrically by determining the voltage-drop across a column of solidified suboxide in a conductivity pipette which had been standardized with mercury. Other suboxides of cesium have been found by Brauer¹ to be good metallic conductors also. Thus these observations definitely show that the suboxide, Cs₃O, still possesses the physical properties of an alkaline metal.

The sample was analyzed by decomposition with water, measurement of the hydrogen evolved, and titration of the total alkali. In this analysis, the suboxide may be regarded as equivalent to a normal oxide plus excess cesium, and the amount of hydrogen evolved on decomposition with water is a direct measure of the excess cesium:



This method is adaptable to the determination of almost any quantity of excess cesium. It has an advantage over the distillation method^{1,4} in that it is not subject to any errors due to volatility of the suboxide and corrosion of the glass by the hot alkaline oxide. A similar procedure for determining excess of metallic barium in barium oxide crystals has recently been described by Libowitz⁵.

II. EXPERIMENTAL

Preparation of Samples

A weighed pyrex capsule of redistilled metallic cesium was placed in a pyrex vessel as shown in Fig. 1. The system was thoroughly degassed by means of a diffusion pump. Dry argon, purified by passage through freshly reduced copper turnings at about 300°C¹, was then admitted to fill the vessel at atmospheric pressure. The vessel was rotated approximately 100° about glass joint J and the tip of the cesium capsule was broken by turning the brass fork, F, about the greased O-ring, O. The glass chips were collected in the side arm, S, for subsequent weighing together with the empty capsule. The brass fork was then pulled out of the way to allow the opened capsule to slide down to the constricted mouth, M, of the central tube. The vessel was slowly rotated back towards the vertical position, and the bottom of the vessel was warmed gently to melt the cesium. Then the argon was pumped out slowly to allow the liquid metal to drip down to the bottom of the reaction vessel. The vessel was again filled with purified argon, and the top part was removed by loosening glass joint K amidst a steady stream of the inert gas. This was replaced by pyrex caps C and D, both previously degassed. After a thorough flush-out, with argon, the tip of cap D was sealed off with a torch, and the argon was pumped out until its pressure dropped to about 0.2 mm. The system was then ready for the admittance of oxygen.

In one experiment, 2.051 g (1.543×10^{-2} mol) of cesium was introduced and allowed to react with 2.572×10^{-3} mol of pure oxygen (prepared by thermal decomposition of pure potassium permanganate or silver oxide, measured and stored up in a gas pipette until ready for use), in the course of about an hour, in the presence of 0.2 mm of argon. The oxygen was admitted slowly in small portions. The reaction took place smoothly and rapidly until about four-fifths of

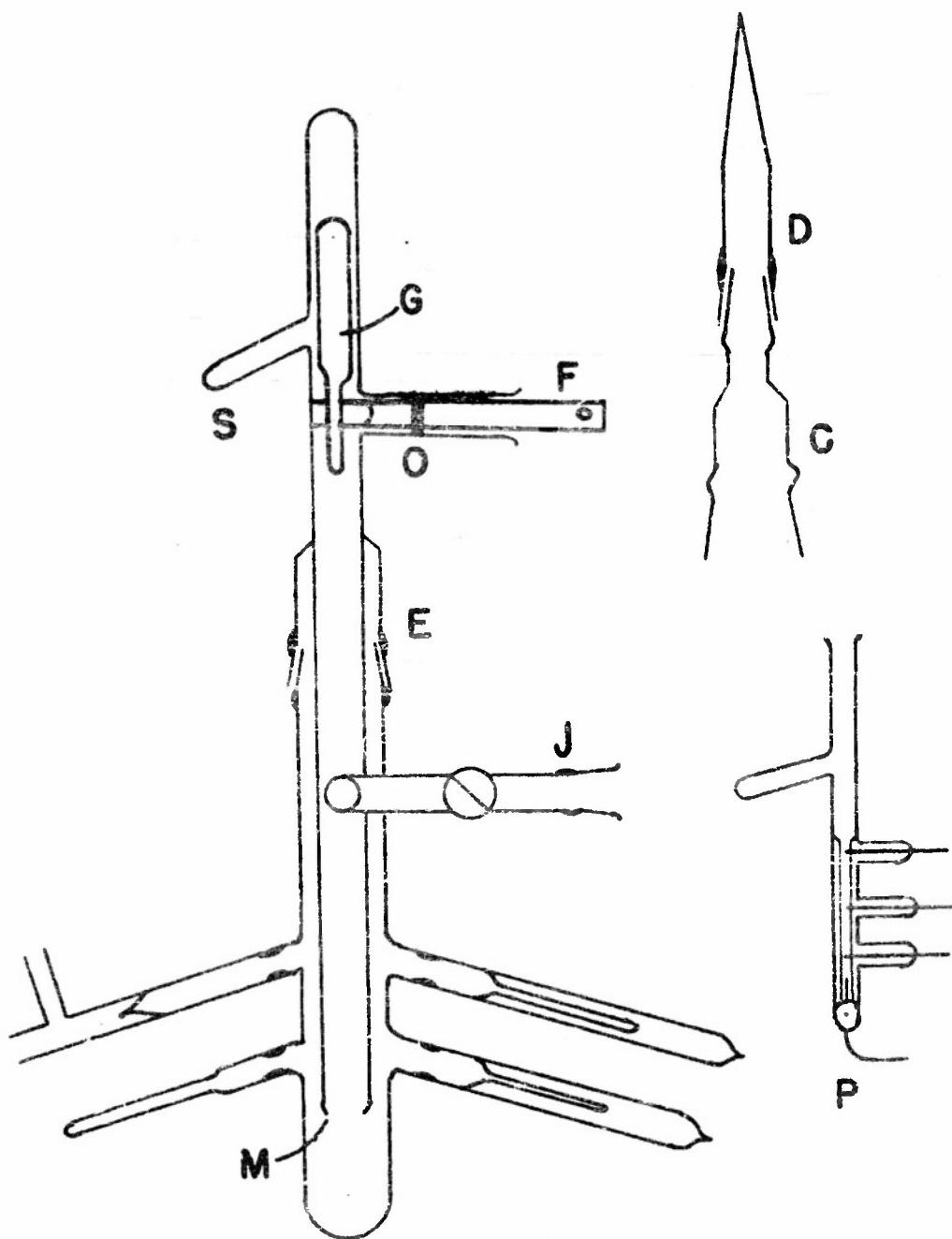


FIG. I. Apparatus for the Preparation
of Cesium Suboxide and Determi-
nation of Electrical Conductivity
of the Sample.

the oxygen had been absorbed and the molten reaction mixture had become coppery red. Then a dark surface layer began to appear. This was decomposed by immersing the reaction chamber in an oil bath at $150 - 170^{\circ}$, and the remaining amount of oxygen was admitted slowly.

The reaction chamber was cooled down to room temperature and filled with argon to a pressure of about 200 mm. (At this stage, a final purification of the argon by passage through a pyrex tubing coated with metallic cesium was necessary to prevent any appreciable superficial oxidation of the suboxide.) Then the stop cock T was closed and the reaction vessel detached from the vacuum system. The reaction mixture was digested in an oil bath at 170°C for an hour, with the reaction vessel inclined and slowly rotated so as to decompose the small amount of higher oxide films with the molten suboxide. The product thus rendered homogeneous was pulverized at room temperature with a long-armed stainless steel chisel (previously degassed) amidst a steady stream of purified argon. The powdered suboxide was loaded into the sample tubes and sealed off under vacuum.

The sample tubes for x-ray powder work were made of thin-walled pyrex capillaries protected by evacuated glass tubing. The tubing was subsequently removed and the capillaries sealed off with a very small flame.

The sample for magnetic measurement was contained in a 5 mm pyrex tubing sealed under vacuum. It was melted by immersing it in a larger tube of hot oil at 180°C and was then centrifuged down to form a compact column of 7 cm height. Owing to the small cross section of the sample, the precision of the measurement was only about 10%.

The sample in the conductivity pipette was also melted and centrifuged down into position. The electrodes consisted of thin platinum wires (30 mil) spotwelded to nonex-beaded tungsten leads; the spot-weld junction and the exposed tungsten part were covered by means of a thin, liquid-tight, pyrex-to-metal seal, then the electrodes were sealed via the nonex beads to the thick-walled pyrex capillary (2.5 mm i.d.). The resistivity-temperature data gave a smooth curve from 0° to 125°C . The measurement was not carried up to the melting point of the suboxide because of a crack which developed at the metal-to-glass seal.

The samples for analysis (about 0.05 gram each) were placed in pyrex capillaries of about 1 mm i.d. These were subsequently broken by means of a magnetic hammer inside a thoroughly degassed pyrex vessel containing about 5 cc of water. The amount of hydrogen evolved was measured by means of a Töpler pump and McLeod gauge, and the alkaline solution was titrated with standard acid by means of a 10 cc micro burette. The sample of the suboxide thus prepared was shown by this analysis to have a composition corresponding to Cs_3O .

The Debye-Scherrer diagrams of Cs_3O , obtained with $\text{CuK}\alpha$ radiation and with $\text{MoK}\alpha$ radiation in an 11.4-cm camera at room temperature, are shown in Fig. 2. The pattern was readily indexed graphically by the simple hexagonal system with a c/a ratio of 0.86.

A highly imperfect crystal of Cs_3O was obtained by melting a small sample of the suboxide in a thin-walled pyrex capillary, allowing it to cool down very slowly to 150°C and digesting it at that temperature for several hours. The crystal was of irregular shape with one hexagonal a-axis approximately parallel to the length of the capillary. Rotation photographs taken with $\text{CuK}\alpha$ radiation and with an a-axis as the rotation axis (Fig. 3) confirmed the hexagonal symmetry with a glide extinction of the $h0\cdot\bar{k}\cdot$ - and $0k\cdot\bar{l}\cdot$ -type with odd k . The y-coordinates of the layer-lines and the x-coordinates of the $40\cdot0\cdot$ and $00\cdot4\cdot$ -reflections gave $a = 8.78\text{\AA}$ and $c = 7.51\text{\AA}$, while the powder data gave $a = 8.78\text{\AA}$ and $c = 7.52\text{\AA}$. The calculated density for two 'molecules' per unit cell is 2.74 g/cc as compared with the observed value of 2.73 ± 0.03 g/cc at 30°C. This density is considerably lower than that calculated for a mixture of $\text{Cs}+\text{Cs}_2\text{O}$ ($d = 3.17$ g/cc, based upon $d(\text{Cs}) = 1.87$ g/cc and $d(\text{Cs}_2\text{O}) = 4.70$ g/cc). This low density again indicates that the suboxide probably is not a lattice compound of metallic cesium in the layer lattice of cesium monoxide although the same metal has been known to form lattice compounds with the layer crystal of graphite⁵.

III. DETERMINATION OF THE STRUCTURE

The presence of strong $hk\cdot\bar{l}\cdot$ -reflections with odd l and the systematic absence of $h0\cdot\bar{k}\cdot$ and $0k\cdot\bar{l}\cdot$ -reflections with odd l show a 11·0-glide, rather than a 11·0-glide, or its equivalent 10·0-glide. Of the eleven hexagonal space groups with a glide symmetry, only D_{3d}^4 , C_{6v} , and D_{6h}^4 give the observed extinction. The unit-cell dimensions and the strong 10·0-reflections eliminate the possibility of putting the six cesium atoms at the combined two and

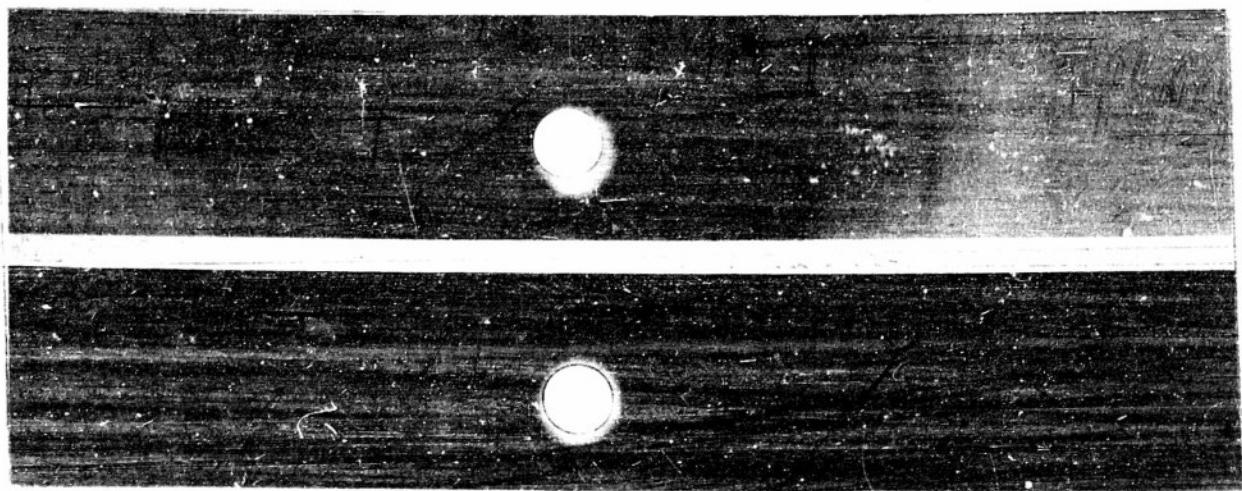


FIG. 2a. X-ray Powder Photographs of Tricesium Monoxide, Cs_3O . Upper Photograph Taken With $CuK\alpha$ Radiation, 113 ma-hr; Sample Prepared by Distilling a Lower Suboxide (Cs_2O_2) in Capillary at $120 - 130^\circ C$. Lower Photograph Taken With $CuK\alpha$ Radiation, 150 ma-hr; Sample Prepared by Direct Combination of the Elements.

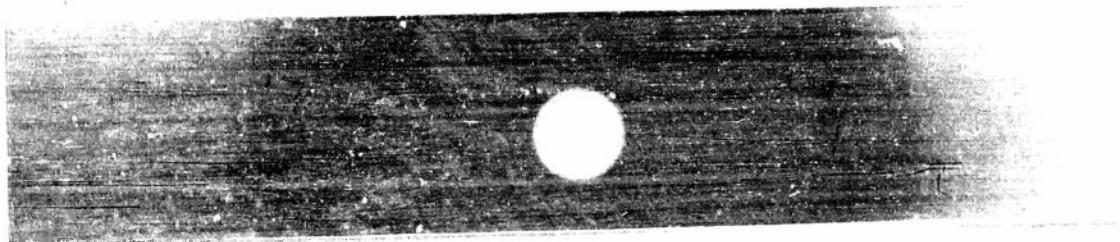


FIG. 2b. X-ray Powder Photograph of Cesium Superoxide, CsO_2 , Obtained as a By-Product (Yellowish Film) in the Preparation of Tricesium Monoxide, Cs_3O .

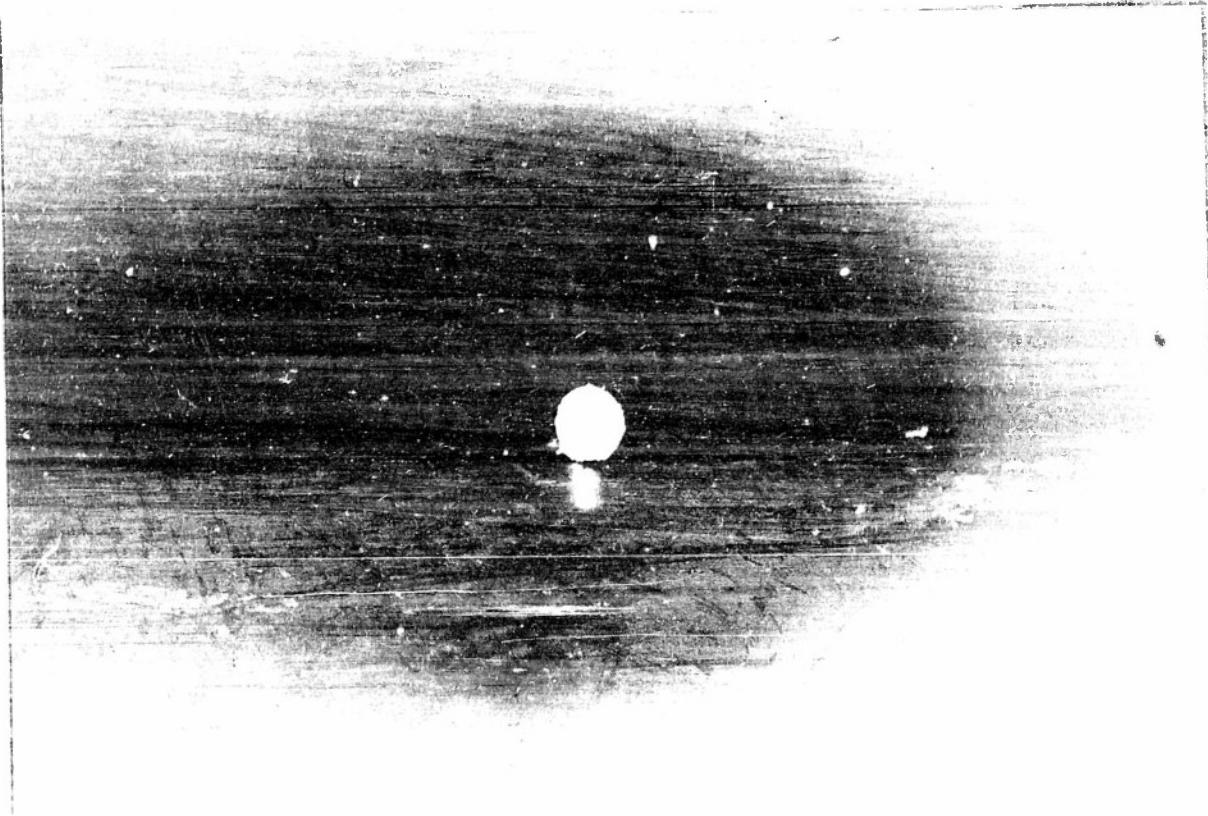


FIG. 3. A-axis Rotation Photograph
of Tricesium Monoxide Crystal.
 $\text{CuK}\alpha$ Radiations, 30 kv,
147 ma-hr.

four equivalent positions possible with this symmetry. Hence the only possibility is the six-equivalent positions. This means that the six cesium atoms in the unit cell of the suboxide are crystallographically alike. If the oxygen atoms exist as oxide ions by taking up four out of the six 6s electrons from the six cesium atoms, then the remaining two 6s electrons must become a common property of the six cesium partial ions in order to make them all equivalent.

Positions of the Six Cesium Ions.

As far as the six cesium atoms are concerned, the three possible space groups, D_{3d}^4 , C_{3v}^2 , and D_{3h}^3 , give the same set of six equivalent positions:

$$\begin{array}{l} u\bar{u}0; \bar{u}0\bar{u}, \bar{u}\bar{u}0; \\ \bar{u}\bar{u}\frac{1}{2}; \bar{u}\frac{1}{2}\frac{1}{2}; u0\frac{1}{2}. \end{array}$$

The relative intensities of the 10.0 and 11.0 powder-lines are approximately in the ratio of 5:1; this fixes u at about 0.24. Comparison of the observed powder-line intensities with that calculated from the contribution of the six cesium ions at different values of the parameter, u , shows that u must lie between 0.245 and 0.255, the intensity contributions from the two oxide ions being small except for the low ordered reflections.

Positions of the Two Oxide Ions.

With $u \neq \frac{1}{2}$ for the 6 Cs, the two oxide ions may have one of the following three sets of equivalent positions:

(1) $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$, for a $C_{632}(D_6^6)$ structure,
with $Cs-O = 3.84\text{\AA}$;

(2) $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$, for a $C_{63/m}(C_{6h}^2)$ structure,
with $Cs-O = 3.35\text{\AA}$; or

(3) $0, 0, \frac{1}{2}; 0, 0, \frac{3}{4}$, for a $C_{6/mcm}(D_{3h}^3)$ structure,
with $Cs-O = 2.89\text{\AA}$.

Comparison of the observed intensities of some of the low-ordered powder-lines with that calculated for the three possible structures with $u \neq \frac{1}{2}$ shows (Table I) that the D_{3h}^3 structure gives the best fit of the intensity data. Based upon this structure and $u \neq \frac{1}{2}$, the calculated intensity distribution for the rotation photograph (Table III) was also found to be in good qualitative agreement with the observed data, though in some cases, such as the 11.0, 11.1, and 11.3 reflections, the absorption corrections appeared to be quite appreciable.

TABLE I. POWDER-LINE INTENSITIES IN RELATION
TO THE POSITIONS OF THE OXIDE IONS

Indices $h k \cdot l$	<u>Relative Intensities Calc.</u>	<u>Relative Intensities Obs.</u>		
	D_6^6	C_{6h}^2	D_{6h}^3	
10·0	35.2	35.2	57.6	60
11·0	9.1	9.1	9.1	10
10·2	14.5	10.8	9.2	10

TABLE II. OBSERVED AND CALCULATED INTENSITIES OF X-RAY POWDER LINES OF TRICESIUM MONOXIDE

Hexagonal Indices hk·l	Plane Spacings		Relative Intensities Observed I _{obs.}	Relative Intensities Calc. I _{calc.}		
	d _{calc.}	d _{obs.}		u = $\frac{1}{4}$ - $\frac{1}{360}$	u = $\frac{1}{4}$	u = $\frac{1}{4}$ + $\frac{1}{360}$
10·0	7.60	7.62	60	62.6	57.6	52.9
00·1	7.52			0	0	0
10·1	5.35			0	0	0
11·0	4.39	4.39	10	8.5	9.1	9.6
20·0	3.801			6.4		
11·1	3.793	3.80	100	69.3	100	100
00·2	3.760	(broad)		24.3		
20·1	3.393			0	0	0
10·2	3.371	3.37	10	10.2	9.2	8.2
21·0	2.875	2.87	15	6.9	17.2	17.0
11·2	2.857			10.5		
21·1	2.684	2.68	50	59.3	65.0	61.6
20·2	2.673			9.2		
30·0	2.535	2.54	2	3.0	3.8	4.4
00·3	2.507			0	0	0
30·1	2.402			0	0	0
10·3	2.380			0	0	0
21·2	2.283	2.28	5	12.1	11.2	10.2
22·0	2.195			1.5	1.5	1.4
11·3	2.176	2.175	5	15.3	15.5	15.7
31·0	2.109			4.1		
22·1	2.108	2.103	5	0	7.0	7.8
30·2	2.101			1.9		
20·3	2.092			0	0	0
31·1	2.031			0	0	0
40·0	1.901			12.2		
22·2	1.896			3.2		
21·3	1.889	1.891	15	21.0	38.8	37.0
00·4	1.880	(broad)		3.7		
40·1	1.844			0	0	0
31·2	1.840	1.833	2	3.4	6.4	6.3
10·4	1.826			3.0		
32·0	1.744	1.74(?)	1(?)	1.4	2.9	3.0
11·4	1.728			1.4		
32·1	1.699			13.3		
40·2	1.697	1.696	10	15.9	29.0	28.8
20·4	1.685			1.4		

* Based upon $a = 8.78\text{\AA}$, $c = 7.52\text{\AA}$.

TABLE III. OBSERVED AND CALCULATED INTENSITIES OF
BRAGG'S SPOTS ON ROTATION PHOTOGRAPHS
OF TRICESIUM MONOXIDE ($C_{53}O$) CRYSTAL

Hexagonal Indices $hk\bar{l}$	Reciprocal Lattice Coordinates ξ	$I_{obs.}$	$I_{calc.}$ (un $\frac{1}{2}$)
01·0	0	2.0	50
02·0}	0		3
00·2}	β		
02·0}	0	4.1	100
00·2}			100
01·2	0	4.6	10
02·2	0	5.7	14
03·0	0	6.1	2
03·2	0	7.3	1
04·0	0	8.2	5
00·4	0	8.3	4
01·4	0	8.4	1
04·2}	0	9.1	6
02·4}	0		46
10·0	1.76	1.0	75
11·0	1.76	3.0	4
11·1	1.76	3.6	63
10·2	1.76	4.2	17
12·0}	1.76	5.1	21
11·2}			
12·1	1.76	5.5	28
12·2	1.76	6.5	6
11·3	1.76	6.8	8
13·0	1.76	7.3	3
12·3	1.76	7.9	9
13·2}	1.76	8.2	3
10·4}			12
21·0	3.52	5*	
20·0}	3.52	2.0	80
21·1}			116
21·0}	3.52	4.1	6
21·2}			20
21·1}	3.52	4.6	54
20·2}			86
21·2	3.52	5.7	5
			14

TABLE III. (Continued)

Hexagonal Indices hk.l	Reciprocal Lattice Coordinates ξ	ζ	$I_{obs.}$	$I_{calc.}(u=\frac{1}{2})$
22.0				
21.3	3.52	6.2	9	24
22.2				
21.3	3.52	7.4	6	38
23.1				
20.4	3.52	8.4	7	26
31.0	(5.27)	1		
31.1	5.27	2.3	77	171
30.0	5.27	3.1	5	16
31.2	5.27	4.2	9	21
31.0				
30.2	5.27	5.1	3	17
31.3	5.27	6.3	7	36
31.2	5.27	6.6	2	6
32.1	5.27	7.4	6	26

* '1' indicates out of range.

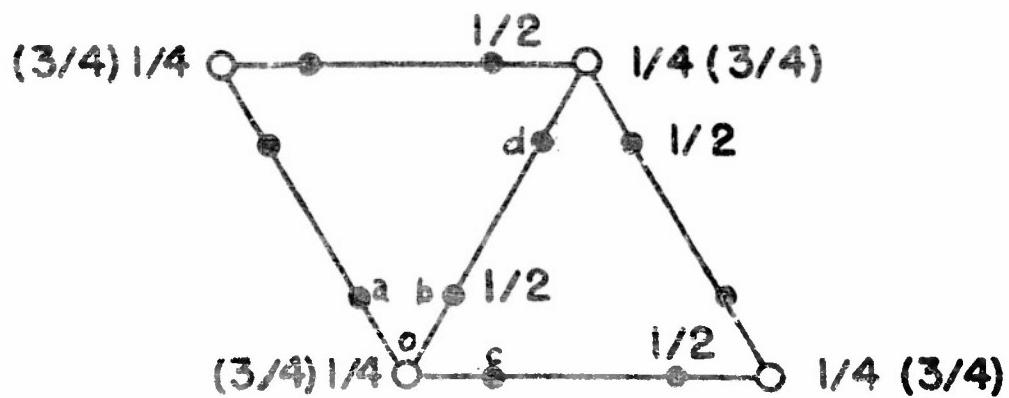


FIG. 4. Atomic Positions of Cs and O in Cs_2O Crystal. Solid Circles Indicate Positions of Cs and Open Circles Indicate Positions of O.

The powder data (Table II) gave: $a = 8.78 \pm 0.01\text{A}$, $c = 7.52 \pm 0.01\text{A}$, $u = 0.250 \pm 0.001\text{A}$, $\text{Cs-O} = 2.89 \pm 0.02\text{A}$, $\text{Cs-Cs}_{(00.1 \text{ plane, bonded to same } O^{\pm})} = 3.81 \pm 0.03\text{A}$, $\text{Cs-Cs}_{(40.0 \text{ plane, bonded to same } O^{\pm})} = 4.35 \pm 0.03\text{A}$, $\text{Cs-Cs}_{(00.1 \text{ plane, bonded to two different } O^{\pm})} = 5.80 \pm 0.04\text{A}$, $\text{Cs-Cs}_{(10.0 \text{ plane, bonded to two different } O^{\pm})} = 5.78 \pm 0.05\text{A}$. Thus the Cs-O distance in Cs_3O is very close to that observed in a cesium monoxide (Cs_2O) layer crystal ($\text{Cs-O}^{\pm} = 2.86 \pm 0.01\text{A}$), indicating that the bond is ionic as expected; while the Cs-Cs distance, where there is no O^{\pm} ion interposed, is about 8% higher than the interatomic distance in metallic cesium (5.80A and 5.78A vs. $2r_{\text{Cs}} = 5.36\text{A}$ at room temperature). Considering the polarizing effect of the oxide ions on the outer shells of the cesium atoms (see Part III of this final report series), some increase in the Cs-Cs distance is to be expected. In conjunction with the observed metallic properties, the observed Cs-Cs distance indicates that the Cs-Cs bonds in Cs_3O crystals are metallic bonds. The structure can be regarded as consisting of hexagonal columns of Cs_3O^+ (formed by piling up the pyrimidal tricesium-oxonium ions, Cs_3O^+ , according to a 6_3 screw symmetry), the columns being bonded together by metallic electrons.

The coefficient of thermal vibration amplitude estimated from the powder data is about $B_p = 10 \times 10^{-16} \text{cm}^2$. This appears to be abnormally large, indicating some sort of lattice defects as was to be expected for such a type of crystal.

It is to be noted that silver subfluoride, Ag_2F , has also been found to possess metallic properties and partial metallic structure in which the Ag-Ag distance is the same as that in metallic silver and the Ag-I distance is the same as that in silver fluoride. Probably this partial metallic character is common to other metal suboxides and subhalides, although the chemistry of this type of compound is yet very little known.

IV. SUMMARY

1. Tricesium monoxide, Cs_3O , has been prepared by the direct combination of cesium and oxygen in the presence of a small amount of inert gas. Experimental technique for handling and analyzing suboxides of cesium has been described.

2. The density, electrical conductivity, and magnetic susceptibility of the suboxide, Cs_3O , have been determined. The suboxide has been found to possess metallic properties.

3. The suboxide has been found, from x-ray single-crystal and powder data, to have a $D_{\bar{h}}^3$ structure with two molecules per unit cell, in which the $Cs-O$ has an ionic bond distance as in the Cs_2O crystal and the $Cs-Cs$ has a metallic bond distance as in metallic cesium. ($Cs-O = 2.89\text{\AA}$ as compared with $Cs-O = 2.86\text{\AA}$ in the Cs_2O crystal; $Cs-Cs = 5.80\text{\AA}$ as compared with $Cs-Cs = 5.36\text{\AA}$ in metallic cesium).

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(See Fig. 1 of Part II for phase diagram.)
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NOTE: In submitting this report it is understood that all provisions of the contract between The Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigator Khi-Puey Tsai Date Sept 15, 1953

Supervisor E. R. Loechte Date Sept 15, 1953

For The Ohio State University Research Foundation

Executive Director Oram C. Wolfert Date 16 Sept. 1953
W.L.H.